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ULTRASONIC VELOCITY AND ABSORPTION IN CARBON DIOXIDE AND ETHYLENE IN THE CRITICAL REGION

by

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Introduction

The present work makes available for the first time ultrasonic data for substances near the critical point. It was undertaken in the hope of adding something to the rather meagre and inexact information available in this important region. More precise information not only of the critical state itself, but of the region about it is especially desirable for its bearing upon the equation of state, for the better understanding of the forces between molecules, and for any light that may be shed on the nature of the liquid state. It is thus seen that the program attempted is larger than the collection of data for use in evaluating the ratio of specific heats, a use to which studies of sonic velocities had largely been limited in the past. The results presented here are encouraging beyond anything that was expected when the study was undertaken.

That the sonic method of investigating thermodynamic problems was far superior to most others, has long been recognized; however, the very high theoretical accuracy of the method has only recently been attained. This is due to the fact that older researches employed audible sound, of wavelengths of large dimensions, thereby necessitating corrections to be applied for the effect of the walls of the apparatus on the sound propagation. These corrections were of dubious accuracy at best. With the development of ultrasonic technique, it became possible for the first time to use wavelengths small in comparison to the dimensions of the apparatus and thereby to eliminate the necessity for wall corrections. Likewise it became easy to avoid diffraction effects by

having a source of sound large compared to the wavelength. The elimination of these troublesome effects with the corresponding freedom from the necessity of applying corrections of uncertain value, has allowed the sonic method, by the use of ultrasonic technique, to realize its innate superiority.

For a gas in the critical region, all the above advantages hold and some new advantages enter in addition. The value of ultrasonic velocity measurement in the critical range avoids one of the chief difficulties encountered in other methods of studying the critical state, namely the abnormally large effect of small amounts of impurities. Investigations, for example, of the difference in density between the two phases as the critical point is approached are influenced by the presence of small traces of impurities all out of proportion to the total amount of impurity present because of the tendency of the foreign substance to concentrate itself in one of the phases. The compressions and rarefactions of an ultrasonic wave-train follow each other so rapidly that there is not much chance for the impurity to redistribute itself between them, and its effect is therefore more in proportion to its abundance.

Then, too, since in general the velocity of sound is given by

$$c^2 = \left(\frac{\partial p}{\partial \rho}\right)_s$$

measurement of the velocity of sound gives directlythe value of a derivative rather than a quantity whose derivative must be estimated.

It follows, then, that for equal accuracy in starting data, higher derivatives must necessarily be more easily and certainly determined for the case of ultrasonic velocity measurements.

Indeed, the indications are that ultrasonic measurements have already outstripped the theorist temporarily, and that the burden is on theory to catch up with interpretation of the facts presented by the method.

Apparatus

Two pressure acoustic interferometers were used. One was an instrument of the movable piston type, used previously by A. H. Hodge. It will not be necessary here to recount a description of this instrument, since it has been described elsewhere (1), (2).

The second pressure interferometer, shown in figure 1, was of the constant path type. It was turned from a solid block of hot rolled steel. The top was held on the chamber by eight 7/8" bolts A.S.E. fine thread. Leak-tight sealing between the chamber and top was accomplished by the standard method of pressing a copper gasket under a V-shaped circular projection from the top. When the bolts were tightened, the copper under the projection flowed enough so that the gasket sealed itself. This pressure unit was designed to be safe at 200 atmospheres and temperatures ranging from -30°C to 150°C, and could probably have been taken up to 300 or 400 atmospheres without any danger save for an unfortunate circumstance. This misfortune was discovered upon testing the chamber at 7000 lbs. per square inch with hydrostatic pressure: water leaked through the

Fig. 1

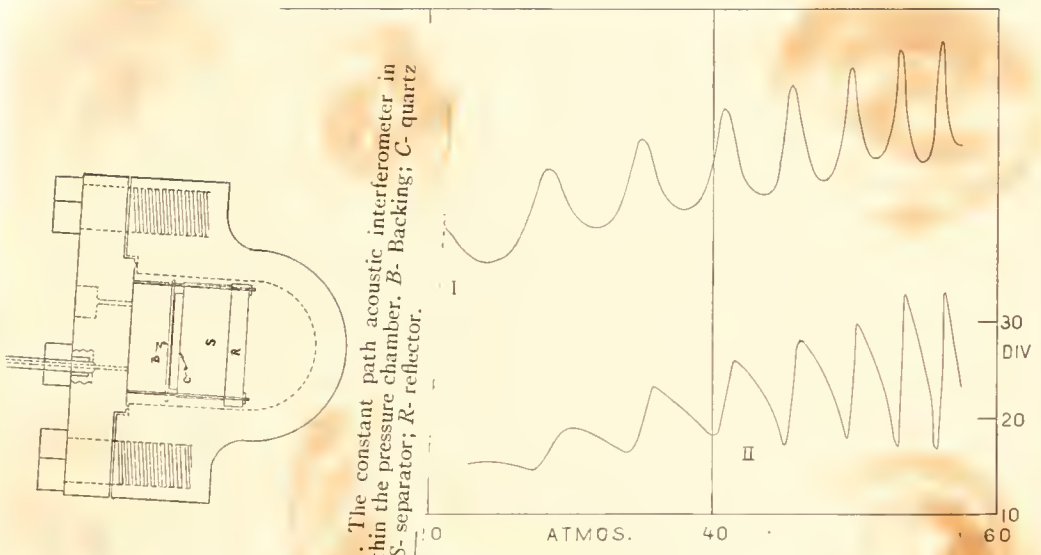

FIG. 1. The constant path acoustic interferometer in place within the pressure chamber. *B*- Backing; *C*- quartz crystal; *S*- separator; *R*- reflector.

D_2 as a function of pressure. Curve I, galvanometer current *vs.* ndenser readings (arbitrary scale) *vs.* pressure to show change n resonance points.

Fig. 1 a

showing an example of the curves obtained in using the constant path interferometer.

dome of the chamber from two well-defined holes. Later, a third leak was discovered in the top, serious enough to make the gas pressure drop about 70 pounds in an hour. Inasmuch as no change in dimensions of the dome could be detected by micrometer calipers during the test up to 7000 pounds per square inch, and from the nature and position of the flaws, it was concluded that they were present originally in the block from which the chamber had been cut. They were probably due to a lapping over of the ends of the ingot during the rolling and were present in the bar when it was bought. Notwithstanding this misfortune, it was deemed safe to use the chamber for low pressures, and it saw use up to pressures of about 1000 lbs. per square inch.

The interferometer unit proper was of fused quartz. The reflector was a circular disc of fused quartz 1 3/4" in diameter and 1/4" thick. Two separators were used interchangeably: both were of fused quartz, 1½" outside diameter and 7/8" inside diameter, but differed in height. The smaller one was 0.2499 inches high; the larger's height was 0.9996" (exactly four times taller). 1/8" slots cut in the separators at the extremities of a diameter, and 1/8" holes bored into the reflector allowed iron rods to be used as supports for the quartz unit. These rods were threaded on both ends; the upper ends screwed into shallow threaded holes in the top of the chamber, while a nut on the lower end of each was sufficient to hold up the quartz parts. The separators were held on the reflector by theforce of gravity alone, so that no expansion or contraction of the supporting rods could change the relative positions of the interferometer parts.

The upper surface of the separator was gold-plated with a negligibly thin film of gold, and the crystal was laid upon this. Both faces of the crystal were likewise gold plated, and the top face was covered by an optically flat disc of pyrex glass with its surface in contact with the crystal also gold plated. Electrical contact could thus be made to the two faces of the crystal. In practice, the bottom face was usually grounded and the high potential was applied to the upper face by means of the gold plated optically flat backing. This backing served another purpose, besides that of making this contact: since it rested on the crystal, it was always nearer to it than an acoustic quarter wave length. Therefore, no radiation from the back of the crystal was allowed to form standing waves and give thereby acoustic reactions which would be confused with the desired ones formed between crystal and reflector.

Two 1/16" holes in the top of the chamber served as gas inlets or outlets; two more allowed thin tungsten wires to be led in to make electrical contact with the crystal. These wires had to be insulated from the chamber, which insulation was accomplished by enclosing them in a thin sheath of pyrex glass. The electrode was made leak proof by leading the wire through an amber cone which fitted into a female conical depression in the lead-in pipe. When the cap was screwed over the top of the electrode, this cone was forced tightly against the walls, and collapsed against the wire, so that no gas could leak out.

Both the gas line and electrode fittings were made of seamless steel tubing 1/4" outside diameter through which ran a hole 1/16" in diameter. Gas-tight contact was made by forcing a male cone on the end of the tubing into a female cone in the top of the pressure chamber by the force of a gland nut on a shoulder on the tubing. This method is, of course, the standard metal to metal seal.

The pressure was measured by an Ashcroft-American gauge which had previously been tested at the Bureau of Standards and found accurate to within 0.5 percent over its entire range (1). The gauge was placed in the line between the gas tank and the interferometer, and a needle valve was so arranged that the line could be closed, having the gauge open to the interferometer but closed to the gas supply.

A standard method was used to drive the quartz crystal. It was placed in parallel with the condensor of a resonant LC circuit which picked up oscillations from a Dow electron coupled oscillator. The current in the resonant circuit was measured by inserting a vacuum thermocouple and feeding the resultant emf. across a type R L and N galvanometer. The frequency of the oscillator was checked by using as standard the carrier waves of local broadcast stations. These stations are required by law to remain within 50 cycles of their assigned frequency and so afford a convenient frequency standard of sufficient accuracy. The station was received on a tuned RF type receiving set and beat against the fundamental or overtones of the oscillator. This beat note was then matched to zero beat with a standard electrically

driven tuning fork. Two such matches were obtained, one for an oscillator frequency higher than the station carrier wave by an amount equal to the frequency of the fork, the other for a frequency lower than the carrier wave by the same amount. The mean reading of the oscillator condenser between these two matches was taken as the setting which would give exact correspondence (zero beat) between oscillator and station. Next, the frequency of the oscillator at each setting was taken roughly by a General Radio wave meter. This allowed one to decide which overtone of the oscillator had given the beat, and the frequency of the setting could thus be determined with an accuracy far surpassing the accuracy of other measurements (as, of pressure) which entered into the readings.

The interferometer during use was kept at a constant temperature in a thermostat filled with transformer oil. This was an iron tank 15" x 15" and 12" deep with a drain pipe in the bottom to facilitate the removal of oil when that was desirable. It was surrounded on all sides except the top by a two-inch layer of glass wool. A metal stirringpaddle kept the oil in the bath well stirred, so that at the temperatures used there was nowhere detectable in the bath a difference greater than $\pm$ .01°C from the temperature at the interferometer. Heat was supplied by several electric light bulbs dipping into the oil. Copper coils allowed the circulation of cool water from the tap; or by means of a small centrifugal pump, ice water could be fed through the coils. The temperature was automatically

maintained at a chosen point by means of a mercury thermal regulator which operated a relay to turn off or on the heating bulbs. Temperature regulation was always obtained by thus balancing the heat from the bulbs against the cooling which resulted from the circulation of cold water, or from radiation losses to the room when the bath was above room temperature. A 50° thermometer graduated in 0.1° which allowed estimations to 0.01° was used to determine the temperatures. This thermometer was checked at 20°C against a thermometer calibrated by the Bureau of Standards and was found to read less than .05° too high. In what follows, this correction has been disregarded.

Temperature readings were taken frequently, and if for any reason the bath temperature was off by more than $\pm$ .05° the condition was corrected and sufficient time allowed for the establishment of thermal equilibrium. Of course, the importance of strict temperature control varied with the region in which the gas was used: at the critical point accurate control was highly important, and every effort was made to keep conditions as constant as possible. Temperature readings were taken always with the thermometer in contact with the interferometer.

The carbon dioxide was obtained from a commercial "bone-dry" tank, reputedly 99.5 percent pure. No attempt was made to purify the gas further, except that the valve was opened and the first pound or so of gas was blown off into the atmosphere. It was then tested for

water vapor by flowing a known volume of the gas as determined by a flowmeter through an absorption tube filled with "Dehydrite" (magnesium perchlorate trihydrate). The carbon dioxide was found to contain slightly less than 0.09 percent water vapor.

The ethylene was of the commercial "anaesthesia" grade, at least 99.5 percent pure and probably 99.7 percent pure, since at the time that the cylinder was bought, the purity of the gas was higher than the medical tolerance. Impurities would be chiefly carbon dioxide and water vapor, and it was attempted to get rid of them in the following way: The ethylene cylinder was surrounded with cracked ice and salt, and allowed to cool for several hours. The valve was then opened and the gas allowed to blow off until a pound or so of pressure had been spent. The valve was then closed and the remainder of the gas used. No attempt was made to analyze it.

Since the pressure delivered by the tanks at room temperatures was usually below that desired, recourse was had to the following method to obtain higher pressures: The bath was cooled some ten degrees or more below room temperature and the pressure chamber and gas cylinder opened to each other. This caused the gas to enter the interferometer and perhaps liquify. After a sufficient time, dictated by experience, the interferometer was closed off from the rest of the system by the needle valve at the pressure gauge, and the bath temperature raised. In this manner, pressures up to 1500 pounds per square inch (the limit of the gauge) could easily be reached.

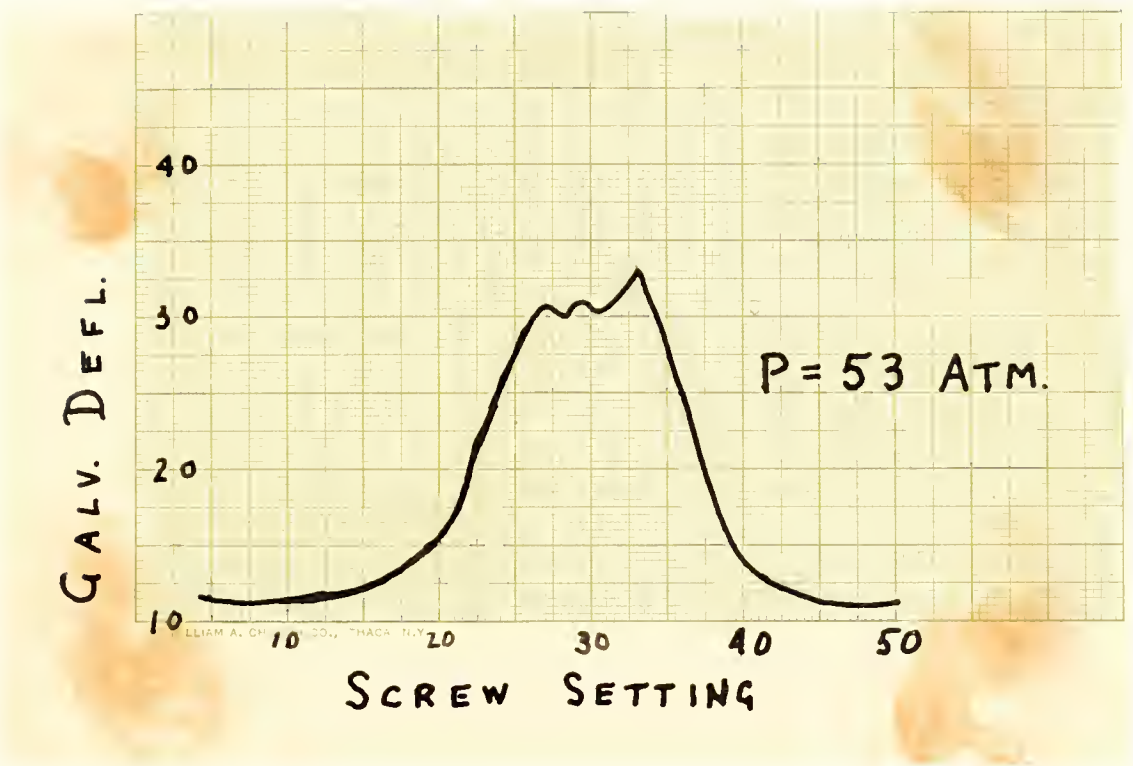

Fig. 2

Appearance of a reaction peak at 53 atmospheres showing structure introduced by overlapping of neighboring crevasses. This peak was clean and symmetrical at lower pressures. Use of such peaks was avoided wherever possible.

The theory of the acoustic interferometer has been given in great detail by Hubbard (3), so that it will be unnecessary here to give more than a brief statement of what occurs in using the instrument: When an alternating potential is applied across the faces of the quartz crystal, the crystal undergoes distortion with a frequency equal to that of the applied electric field. The crystal, upon undergoing this distortion, develops (by the converse piezoelectric effect) charges on its faces opposite to those causing the distortion, so that a vibrating crystal may be regarded as a source of back electromotive force. The magnitude of this back emf. depends on the amplitude of the vibration, which is usually very small. However, if the frequency of the driving oscillator coincides with a natural frequency in the quartz crystal, the amplitude increases to comparatively high values and the back electromotive force increases greatly. The current in the driving circuit drops to a low value, which drop is known as a crevasse. The depth of this crevasse changes whenever the amplitude of the crystal changes; the greater the damping of the crystal, the higher is the crevasse. (Analogous statements are, that the back emf. is smaller; or, that the current in the resonant driving circuit has a higher value).

Consider now a fluid column coupled to the crystal and terminated by a solid reflecting wall. If the distance between the crystal and reflector be an integral number of half wavelengths, standing waves will be formed by the sound emitted or reflected from the source and that reflected from the reflector. This condition corresponds

to a maximum of transfer of energy from the crystal to the fluid and gives maximum damping of the crystal, wherefore the bottom of the crevasse is higher than it would be were the distance unfavorable for standing waves.

If the reflector be moved backward or forward this condition of resonance will be destroyed and the crevasse bottom will fall until the reflector reaches another distance from the crystal corresponding to $\left(\frac{n \pm 1}{2}\right)\lambda$, when the crevasse bottom will rise again. The current in the resonant circuit will thus increase sharply to a maximum at positions of the reflector corresponding to half wavelength separation. By measuring the distance through which the reflector is moved, the wavelength is determined, and if the frequency is also known, the velocity can be calculated. This is the basis for the piston - (movable reflector-)type interferometric measurements.

The working of the constant path interferometer may be described as follows:

After standing waves have been set up in the fluid column between source and reflector, suppose that the wavelength of sound in the fluid be altered, as by changing the pressure. It is clear that as the pressure change progresses, the standing wave system will soon disappear, and likewise the resonant circuit current will drop. Continued change in pressure eventually causes the wavelength to alter enough so that now one more or one less half wave fits into

the distance between crystal and reflector. This again causes the resonant circuit current to rise; at its maximum value the standing waves are completely restored. By noting the pressures at which these maxima occur, the velocity of sound may be calculated at that pressure from a knowledge of the wavelength, which may be obtained if the number of half waves fitting into the source to reflector distance is known.

To determine this number of half waves, it is necessary to know the velocity of sound at some one pressure from independent data, which allows of the calculation of the number at that point. The number at any other pressure can then be arrived at by counting the number of reaction peaks from the known "reference" pressure to the pressure at which it is desired to determine the velocity, since each peak corresponds to the appearance or disappearance of a half wave. It should be noted, since the reference velocity serves only to indicate the number of nodes in the interferometric distance, that the accuracy of the measurements obtained is in no wise limited by the accuracy with which the reference velocity is known, provided that this be not grossly in error. A simple example will make this clear: suppose that at one reaction peak maximum, calculation from independent data were to show 62.07 nodes in the distance. Such a number is impossible, for a reaction peak maximum corresponds to an integral number of half waves. The true number would be considered as 62.0 and the fraction, ascribed to error in the independent data, would be dropped. By this procedure the error in the auxiliary data is automatically ruled out.

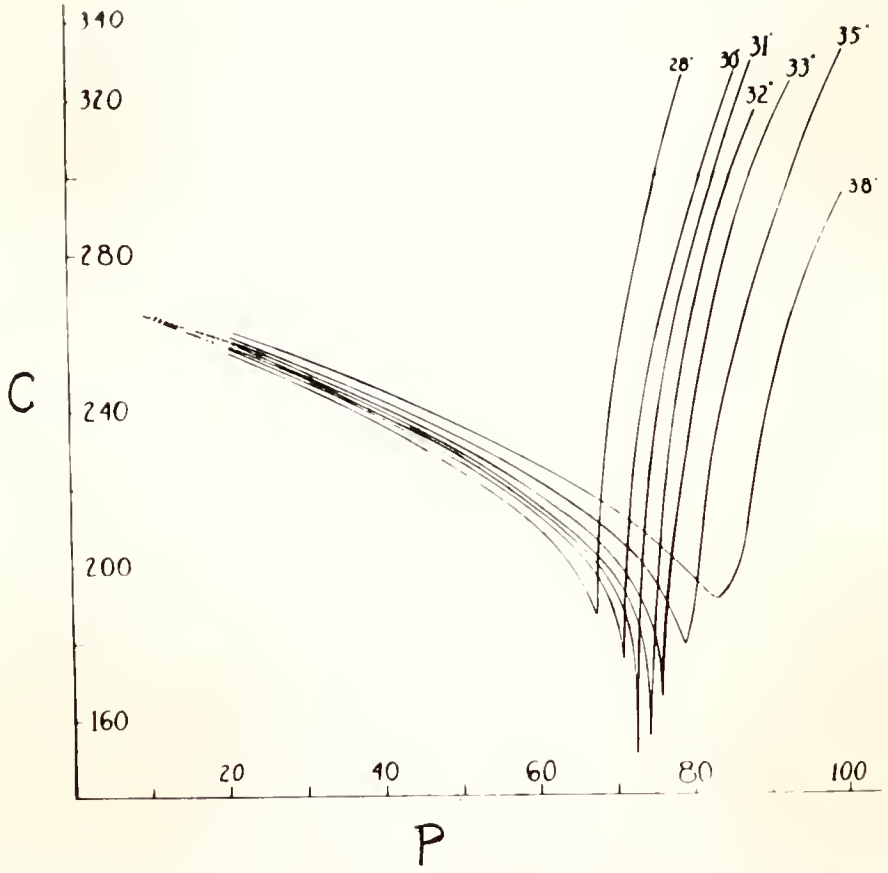

Fig. 3

Velocity of sound in carbon dioxide vs. pressure with temperature constant

It was found experimentally in this laboratory that boundary losses of a dissipative nature occur on reflection. The theory based upon this effect by K. F. Herzfeld (4) shows that, upon reflection at a gas boundary, a sound wave undergoes a small change of phase and of amplitude because of dissipative energy loss. This results in an effective increase in path length of the acoustic interferometer which introduces a slight inaccuracy in the velocity determination. It is possible to eliminate this by using two different path lengths; however in the present work, the inaccuracy was so small as compared to other sources of error that it was disregarded.

Procedure

a) With the piston type interferometer

After the gas had been brought up to the desired pressure and the bath was at the correct temperature, about an hour was allowed for thermal equilibrium to be established. Meanwhile, the oscillator was turned on, and an equal length of time allowed for it to stabilize itself. Sometime during the run, either at the beginning or end, or both, a check was made on the frequency of the oscillator. The frequencies obtained from day to day all fell within an extreme of 500 cycles of one another and usually were different by less than 200 cycles.

When everything was ready, the oscillator was set on a crevasse and the condenser in the resonant circuit was adjusted so as to make this crevasse as symmetrical as possible. This adjustment

was sometimes futile, as will be explained later. The piston was then read at three settings near the crystal, and three farther out by ten to twenty wavelengths. These six readings were sufficient to give wavelength values agreeing with each other to 0.00002 cm (one part in 3000) in the best cases. At other times the agreement was not so good, due to matters to be discussed later. The pressure was then reduced to another desired point, time was allowed for the re-establishment of equilibrium, the crevasse adjustments were remade, and another set of piston readings taken.

b) With the constant path interferometer

The pressure was brought up and equilibrium established as before. A suitable crevasse was found, and adjustments were made for symmetry. The gas was then allowed to leak out very slowly, while by simultaneous adjustments of resonant condensor and the vernier condenser of the oscillator, the crevasse was kept symmetrical and its bottom followed. Simultaneous readings were then taken of the current in the resonant circuit (as followed by the galvanometer), of the pressure, and of the vernier oscillator condensor. The peaks in the resonant circuit current indicated pressures at which the standing wave system was established.

To determine whether the velocity was increasing or decreasing, recourse can be had to one of two methods: If the current be plotted against the pressure, the spacing of the peaks will show in which direction the velocity tends: a closer spacing of peaks towards higher pressures means that the velocity is decreasing (i.e. the number of peaks is increasing as pressure increases).

Another method of arriving at the same conclusion is to plot the vernier condenser readings against pressure along with the current-pressure plot. The capacity-pressure plot has the nature of a dispersion curve and mirrors a very small frequency change of the quartz crystal. If the velocity is decreasing, the maxima in the capacity-pressure plot will lag the resonance peaks; if velocity is increasing, these maxima will lead the peak.

One of the first things which became apparent as work progressed was the behavior -- or, almost, misbehavior -- of the quartz crystals under pressure. The crevasse frequency shifts slightly, as the pressure increases, but this is generally a slight matter, amounting to about 500 cycles in going from 1 to 100 atmospheres. Concurrent with this is the more serious matter: The crevasse grows broad and shallow, and is overlapped by neighboring crevasses. This has the effect of broadening the reaction peak and introducing structure into it. This were still not so bad for velocity measurements (though fatal for absorption of sound measurements), except that since the various parts of the structure correspond to slightly different frequencies, their relative position changes in a degree depending on how far apart in frequency they originally were. It is this which was one of the chief causes of inaccuracy mentioned before. Its seriousness was overcome by using the crevasses which kept to a fair degree their simplicity over the entire path of the piston; or failing that, using a crevasse which was good over some range, and

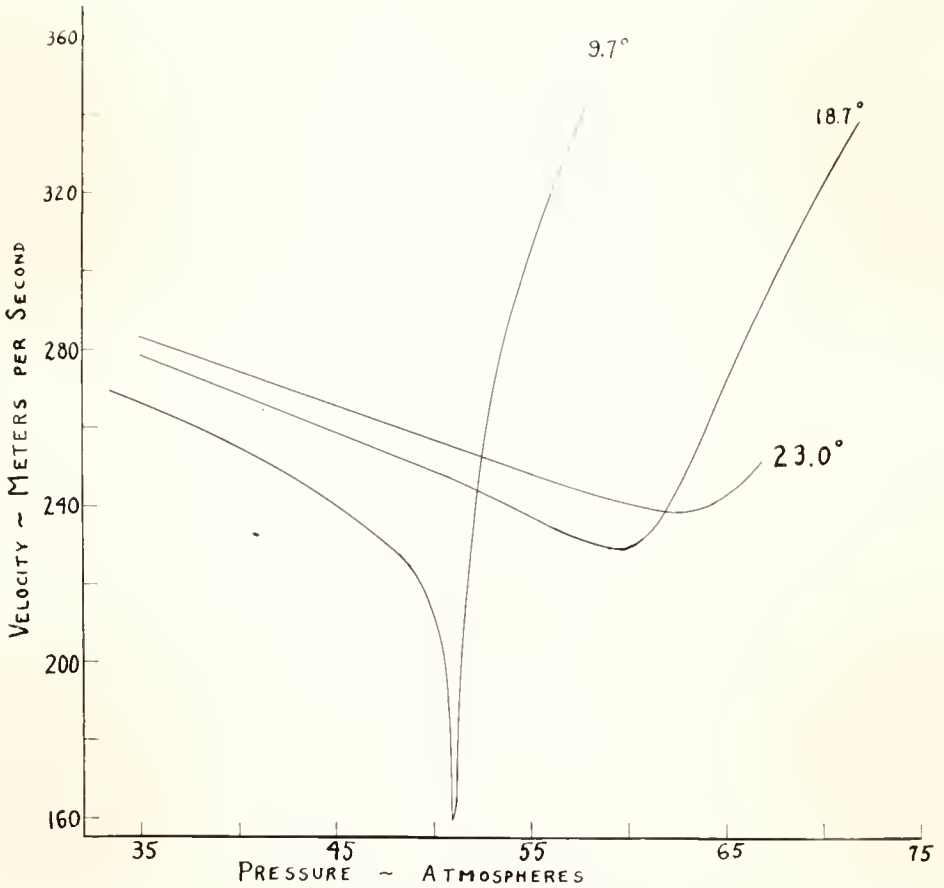

Fig. 4

Velocity of sound in ethylene as a function of pressure with temperature constant

then shifting to another which was good over the next range of pressure investigated.

The figures show what becomes of a sharp clean reaction peak at low pressures (1-10 atm.) when the pressure is increased to 50 or 60 atmospheres.

In the higher range of pressures, the crevasse often vanishes completely, and then the interferometer gives the liquid type of reaction (6,7). This consists of the appearance of a sharp dip in the resonant current circuit at reflector settings $\left(\frac{2n + 1}{4}\right)\lambda$; the current at other settings of the reflector maintains a steady high value. The appearance of this dip reaction depends on the radiation resistance of the fluid, and on the coupling between fluid and the particular mode of vibration causing the crevasse. The dips usually show as bad structure as the peaks, although dips can be found which are as reliable as the best of peaks. The velocities reported were taken with one of the two kinds of reactions, depending on which gave the most consistent values for wavelength in the working range.

Results

The velocity of sound in CO_2 and ethylene was taken as the gas followed a pressure-volume isothermal. The values are recorded in the accompanying tables, and the figures illustrate the same data.

As is well known, CO_2 exhibits molecular dispersion of sonic velocity in a range of frequencies which includes those used

for this investigation, and that accompanying this dispersion is a high absorption of sound. Lest the trend of the velocity-pressure curves be wrongly attributed to this effect, it must be pointed out that this is not the case. The dispersion is intimately connected with the number of collisions of fluid molecules necessary for equilibrium of energy to be established between translation and the inner degrees of freedom: some time t will be necessary on the average for a molecule to make a surficient number of collisions for such excitation to occur. Now if the sound pulse passes in a time larger than t (low frequency), then equilibrium will always obtain; if the passage occurs in a time smaller than t (high frequency), again equ librium will obtain, except that in this latter case the inner degrees of freedom will fail to be excited, and the fluid will behave as though it had a higher rati of specific heats. Between these two extremes there will be a gradual transition from the lower to the higher velocity accompanied by an anomalously large absorption of sound. Now, if the pressure be increased, the number of collisions per unit time will be increased, and t will be decreased. This means that a frequency which was too fast at low pressures, finds itself becoming effectively slower, i.e. the increased pressure allows the gas to attain energy equilibrium in a shorter time and to look on the once fast frequency as a slow one. For CO_2, this condition was realized when a pressure of about ten atmospheres was attained, above this pressure no high absorption due to molecular dispersion of sound was noticed.

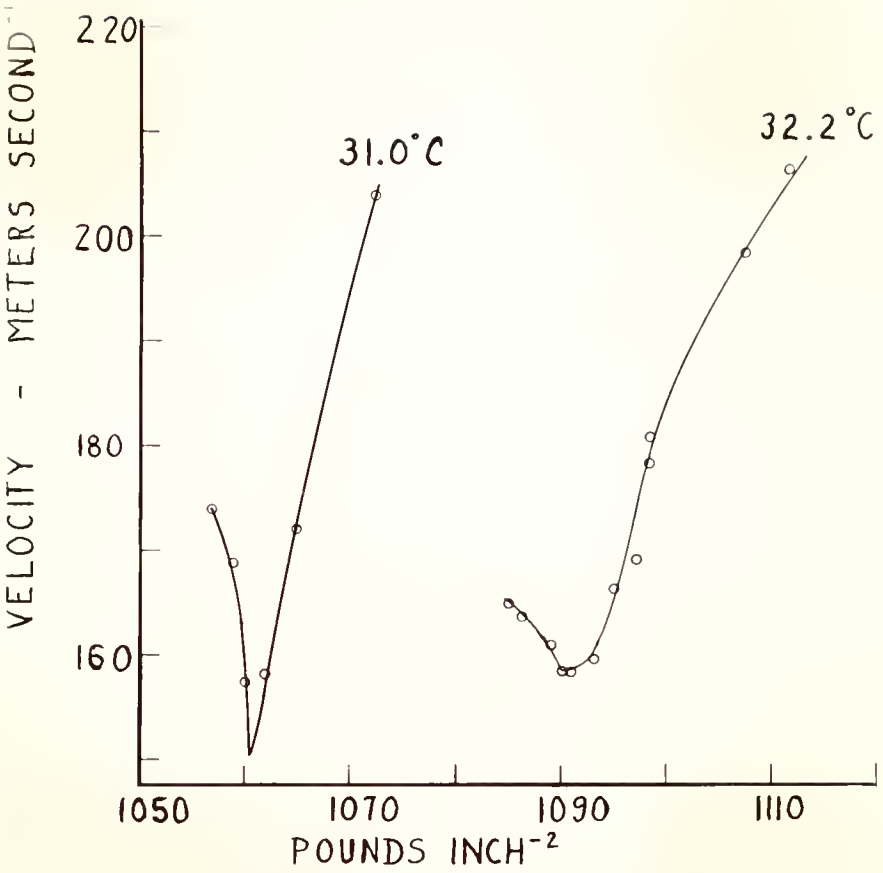

Fig. 5

Large scale plot of velocity of sound in carbon dioxide showing the cusp-like form of the minima

A further point is that ethylene, a non-dispersive gas, showed the same velocity-pressure trend as did CO_2 and, if argument by analogy be permitted here, this furnishes additional evidence that whatever the cause of the trend, molecular dispersion can be ruled out.

Furthermore, ratios of specific heats determined from Hodge's (2) velocity measurements in CO_2 at 23°C and from one to 60 atmospheres check excellently with the few values found by static.

When the general tenor of the velocity-versus-pressure curves had been determined, an attempt was made to find out in more detail the structure of the curves at the minimum. On the condensed scale on which they are drawn, the minima, at least for the lower temperatures, look very sharp, as though there were a discontinuity in slope.

The 38° velocity-isothermal was first investigated. It must be remarked that the apparatus did not lend itself too well to such close investigation due to the difficulty in reading the small pressure differences on the gauge. Nevertheless it appeared that the 38° curve was continuous in slope through the minimum.

Since a discontinuity was to be expected at some temperature not too high above the critical temperature according to the theory of Mayer and Harrison (5), the nature of the minimum at 32.2°C was investigated. An attempt was first made to effect small changes in decreasing pressure by flowing out measured volumes of gas. The gas was collected by displacing oil from a graduated cylinder; about 100 cc

was removed, a velocity reading taken, and the process repeated. It was hoped in this way to obtain a curve the points of which would be consistent with each other, and not depend upon observational error attendant upon deciding what was the gauge pressure. The ordinate was velocity, the volume flowed out was the abscissa. This abscissa was of course a very unusual one, and made it a severe test indeed to detect any discontinuity, since the scale became widely expanded just in the interesting region and thereby had a tendency to mask any discontinuity which might be there. In fact, the curve so obtained was such as to allow one to read in a discontinuity or to rule it out, depending on the prejudice of the judge. However, during the run, pressure readings had been taken from time to time which, while subject to gauge errors, were consistent with one another, and a plot of velocity vs. this carefully determined pressure could be made. As may be seen from the figure, the curve so obtained had a discontinuity in slope at the "gaseous" side, and a continuous slope on the "liquid" side.

Velocities below the critical temperature show discontinuities in slope for that pressure at which liquifaction set in. It may be expected that these curves should show also an actual discontinuity in velocity at the liquifaction pressure; however, this discontinuity was not observed experimentally. It seemed that velocity readings could be taken as close as desired to the minimum on either side and still yield a curve not discontinuous in itself, but discontinuous in the first derivative.

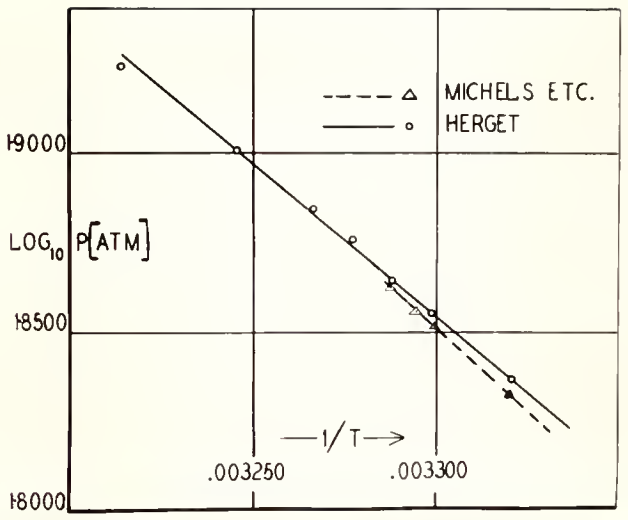

Fig. 6

Log of pressure (in atmospheres) vs. 1/T for the minima of the velocity of sound curves for carbon dioxide

While the velocities reported are self consistent, except at the minimum of the velocity-pressure curve through the critical point, to ± 0.05 percent, their absolute accuracy, because of limitations of the gauge, was ± 0.5 percent. Just at the critical point of both gases investigated, the reaction peaks showed a striking unsteadiness, giving evidence of a state of confusion in the gas in the interferometer chamber. This was doubtless produced by the well known density fluctuations which occur in a gas at the critical point. In addition, ethylene at its critical point showed a high scattering of sound, making it impossible to obtain any evidence of the sound field at distances from the crystal of more than five or six wavelengths.

It is obvious from this, that the error in the velocities just at the critical point is larger than the ± 0.5 percent error ascribed to the rest of the readings. For carbon dioxide at the critical point, the error is ± 2.0 percent; for ethylene at the critical point, the error is ± 3.5 percent. This region of larger error extends about one quarter atmosphere on either side of the minimum in each case.

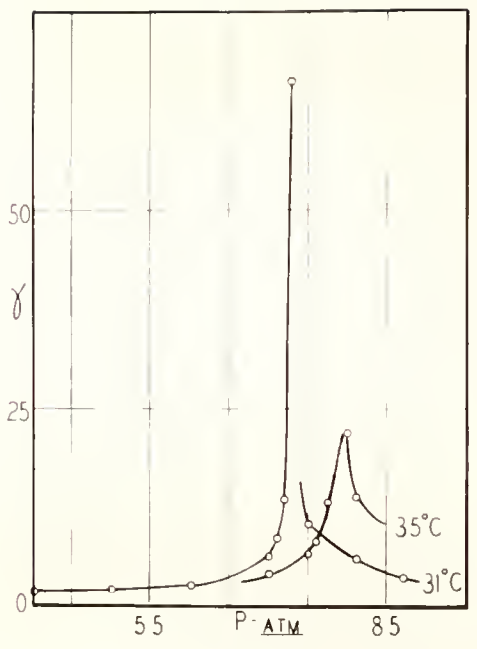

Fig. 7

Ratio of specific heats for carbon dioxide vs. pressure for 31°C (critical temperature) and 35°C, as calculated from the velocity of sound in conjunction with Amagat's pv data.

Carbon dioxide. Temperature, 28.0°C

Frequency Kilocycles	Velocity Meters/sec.	Pressure Atmospheres	Frequency Kilocycles	Velocity Meters/sec.	Pressure Atmospheres
266	317.6	77.50	287.5	186.2	68.27
266	310.7	77.17	226	188.9	68.00
266	303.2	75.95	266	192.9	67.04
287.5	301.4	75.86	266	193.3	66.90
287.5	291.2	74.39	266	197.4	65.61
287.5	278.6	73.60	266	199.3	65.12
287.5	251.9	70.49	266	203.6	63.50
266	242.8	70.00	266	214.2	57.79
266	226.9	69.18	266	226.1	49.35
287.5	(225)	68.95	266	239.4	37.80
287.5	184.0	68.65	266	255.3	20.59
226	186.9	68.27	266	265.3	8.76

Carbon dioxide. Temperature, 30.0°C

285.5	324.8	85.60	266	183.3	71.09
285.5	303.9	81.20	266	186.5	70.62
285.5	261.9	76.41	266	188.4	70.50
285.5	222.8	74.81	276.5	190.4	70.21
285.5	209.9	72.53	291	190.1	70.21
266	186.4	72.01	266	189.6	70.18
283	187.2	72.01	291	208.4	63.22
260.2	189.7	71.93	266	220.5	55.13
266	186.4	71.86	266	238.5	38.41
266	187.6	71.86	266	246.7	31.80
287.3	182.0	71.79	266	249.6	28.72
266	177.2	71.71	266	257.9	20.03
266	177.4	71.62	266	264.9	10.73

Carbon dioxide. Temperature, 31.0°C

Frequency Kilocycles	Velocity Meters/sec.	Pressure Atmospheres	Frequency Kilocycles	Velocity Meters/sec.	Pressure Atmospheres
266	329.3	88.10	266	210.4	63.10
266	310.0	84.98	266	211.9	62.40
266	286.0	81.18	285.5	213.6	60.58
267.9	291.4	80.85	266	219.8	57.72
266	239.0	76.27	266	234.8	45.14
266	223.5	75.19	285.5	239.7	39.97
266	210.7	74.60	266	240.4	39.49
274.1	203.6	73.95	266	245.6	33.17
274.1	172.0	73.48	266	247.8	31.73
274.1	158.3	73.25	266	250.9	28.47
266	150.1	73.17	266	254.3	24.94
274.1	157.3	73.16	266	254.7	24.13
274.1	168.8	73.09	266	256.3	21.61
274.1	173.9	72.96	266	259.2	17.39
274.1	178.0	72.81	266	261.5	14.54
266	182.8	72.48	266	264.6	12.43
266	200.7	68.22	266	265.4	10.19

Carbon dioxide. Temperature, 32.0°C

287.5	340.2	93.00	266	172.7	74.58
266	315.6	88.40	266	173.4	74.41
266	279.3	81.60	266	191.7	72.39
266	261.7	80.38	266	214.9	61.32
266	243.3	78.65	266	233.8	46.70
287.5	225.8	77.21	266	241.0	39.59
266	219.3	77.19	266	247.1	33.17
266	197.8	76.04	266	248.5	31.73
266	182.7	75.79	266	254.6	25.01
266	170.7	75.44	266	255.2	24.87
287.5	177.4	75.20	266	255.6	23.51
266	154.8	75.10	266	257.5	21.68
287.5	156.1	75.02	266	259.5	18.55
266	167.9	74.99	266	262.1	14.54
287.5	169.6	74.58	266	264.2	12.50

Carbon dioxide. Temperature, 33.0°C

Frequency Kilocycles	Velocity Meters/sec.	Pressure Atmospheres	Frequency Kilocycles	Velocity Meters/sec.	Pressure Atmospheres
266	323.0	92.85	266	206.2	68.35
266	306.6	88.00	266	216.1	62.29
268	292.7	87.41	266	228.7	51.75
266	264.7	82.92	285.5	231.1	48.89
266	205.9	78.17	266	240.1	41.80
266	193.9	77.68	266	249.3	31.67
266	187.3	77.40	266	252.5	28.41
266	170.6	77.20	266	254.7	25.01
266	167.8	76.78	266	255.5	24.95
266	166.9	76.64	266	258.2	21.41
266	172.1	76.40	266	257.9	21.34
266	182.5	75.87	266	260.6	17.39
266	182.7	75.49	266	263.8	13.11
266	197.3	72.30	266	264.9	12.50
266	206.3	68.40	266	266.2	11.14
			266	270.4	5.97

Carbon dioxide. Temperature, 35.0°C

266	331.8	99.58	266	184.2	78.58
266	313.9	95.71	266	187.6	77.99
266	300.4	93.06	266	189.2	77.56
266	267.9	87.79	266	196.7	75.61
266	221.6	83.14	266	198.5	75.59
266	212.0	82.17	266	204.2	72.48
266	196.3	81.30	266	211.2	67.93
266	187.5	80.77	266	218.1	62.87
266	183.3	80.43	266	213.7	51.94
266	181.0	80.16	287.5	239.2	42.19
266	179.7	79.67	266	241.4	42.19
266	180.2	79.48	266	249.0	33.17
266	179.2	79.48	266	251.4	31.26
266	180.4	79.41	266	267.3	11.14

Carbon dioxide. Temperature, 38.0°C

Frequency Kilocycles	Velocity Meters/sec.	Pressure Atmospheres	Frequency Kilocycles	Velocity Meters/sec.	Pressure Atmospheres
266	249.4	99.63	266	192.1	83.87
266	261.3	92.65	266	193.0	82.40
266	215.4	87.61	266	196.3	80.87
268.1	209.1	87.00	274.2	198.4	80.72
267.9	194.0	85.28	268.1	201.4	79.13
266	193.5	85.21	266	207.5	74.63
267.8	192.3	85.07	266	212.3	71.83
267.9	192.2	84.70	266	224.3	62.22
274.2	193.4	84.70	274.3	232.3	53.90
273.2	192.3	83.40	275.2	243.0	42.88
			266	247.7	37.65
268.1	193.0	83.33	266	268.0	11.14

Ethylene
Temperature 9.7°C
Frequency - 274.1 kilocycles

Velocity Meters/sec.	Pressure Atmospheres	Velocity Meters/sec.	Pressure Atmospheres
348.5	58.48	165	51.06
318.0	56.97	162	51.06
309.0	55.30	160	50.98
298.6	54.59	193.0	50.76
290.0	53.97	202.8	50.65
280.8	53.41	222.0	49.16
263.0	52.95	239.1	45.21
225.0	51.67	247.6	42.47
196.2	51.26	265.3	35.27

Ethylene
Temperature - 18.7° C
Frequency - 274.1 kilocycles

335.4	71.77	234.1	61.44
325.6	70.55	232.4	61.13
322.8	70.38	229.3	60.37
311.5	69.19	228.7	59.62
306.5	68.48	229.6	58.81
300.3	67.79	230.6	58.19
275.5	65.61	236.8	55.06
254.8	63.62	247.2	50.71
246.5	62.90	261.5	43.65
240.4	62.22	276.8	35.68

Ethylene
Temperature - 23.0°C

Frequency Kilocycles	Velocity Meters/sec	Pressure Atmospheres	Frequency Kilocycles	Velocity Meters/sec.	Pressure Atmospheres
274.1	249.9	66.78	598.0	253.1	51.84
274.1	246.3	66.18	598.0	257.4	49.69
274.1	242.1	65.00	274.1	261.1	47.58
274.1	240.3	64.38	598.0	261.5	47.43
274.1	237.7	62.88	598.0	266.4	44.60
274.1	237.2	61.67	598.0	271.1	41.92
274.1	238.4	61.06	274.1	272.1	41.34
274.1	240.7	59.50	598.0	273.6	40.58
274.1	244.2	56.98	598.0	276.1	39.19
598.0	249.0	54.19	598.0	278.6	37.67
274.1	256.1	52.80	274.1	281.6	35.74

The minima of sound velocity occur at temperatures and pressures which below the critical point, as would be expected, fall on the p,t equilibrium curve of liquid-vapor. Above the critical point the temperatures and pressures of the sound velocity minima form a natural continuation of the same curve, as predicted from thermodynamics by Lucken.(8). This becomes evident on inspection of the figure. Interest in this subject has been greatly enhanced by the recent work of Professor J. E. Mayer and his students (9), who have approached it from the point of view of statistical mechanics. The figure shows two isotherms of the ratio of specific heats of CO_2 calculated from the values of sound velocity and the pv data of Amagat.(10). These are included as an illustration of the marked deviations of such quantities at the critical point and near it.

During a run, attempts were often made to obtain data for absorption and reflection coefficients. These attempts were usually frustrated by the bad structure of the reaction peaks already discussed. However, three sets of data were obtained which showed sufficient consistency to warrant use. The information was obtained for carbon dioxide and is shown in the table. The values given for the absorption and reflection coefficients are probably correct to $\pm$ 20 percent.

A is defined by $A = \mu/\lambda^2$ where μ is the classical acoustic absorption coefficient given by $I_x = I_o e^{-\mu x}$. γ^* is the intensity coefficient of reflection.

Temperature	Pressure	Frequency	A	γ^*
24.5°C	54.4 atm.	274.6 kc	.022	.79
38.0°C	53.9	274.6	.0032	.96
38.0°C	43.1	274.6	.0049	.96

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V I T A

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